

CLAIMS

1. A film represented by the formula $\text{Si}_v\text{O}_w\text{C}_x\text{H}_y\text{F}_z$, where $v+w+x+y+z = 100\%$, v is from 10 to 35 atomic%, w is from 10 to 65 atomic%, y is from 10 to 50 atomic%, x is from 2 to 30 atomic%, and z is from 0.1 to 15 atomic%, wherein substantially none of the fluorine is bonded to the carbon.
2. The film of claim 1, wherein most of the hydrogen is bonded to the carbon.
3. The film of claim 1, having a dielectric constant of less than 3.5.
4. The film of claim 1, having a dielectric constant of less than 3.0.
5. The film of claim 1, having superior mechanical properties to an OSG film stoichiometrically equivalent to the film but for the absence of fluorine in the OSG film.
6. The film of claim 1, having a bulk density of less than 2.0 g/cc.
7. The film of claim 1, having a bulk density of less than 1.5 g/cc.
8. The film of claim 1, having a pore size less than 5 nm equivalent spherical diameter, as determined by small angle neutron scattering or positron annihilation lifetime spectroscopy.
9. The film of claim 1, having a pore size less than 2.5 nm equivalent spherical diameter, as determined by small angle neutron scattering or positron annihilation lifetime spectroscopy.
10. The film of claim 1, deposited on a semiconductor substrate.
11. The film of claim 1, provided as an insulation layer, an interlayer dielectric layer, an intermetal dielectric layer, a capping layer, a chemical-mechanical planarization or etch stop layer, a barrier layer or an adhesion layer in an integrated circuit.
12. The film of claim 1, having an average weight loss of less than 1.0 wt%/hr isothermal at 425°C under N_2 .

13. The film of claim 1, having an average weight loss of less than 1.0 wt%/hr isothermal at 425°C under air.

14. The film of claim 1, having a bulk density of less than 1.5 g/cc, a pore size less than 2.5 nm equivalent spherical diameter, as determined by small angle neutron scattering or positron annihilation lifetime spectroscopy, wherein most of the hydrogen is bonded to the carbon, and the film is deposited on a substrate as an insulation layer, an interlayer dielectric layer, an intermetal dielectric layer, a capping layer, a chemical-mechanical planarization or etch stop layer, a barrier layer or an adhesion layer in an integrated circuit.

15. The film of claim 1, wherein $x/z > 0.25$.

16. A film represented by the formula $\text{Si}_v\text{O}_w\text{C}_x\text{H}_y\text{F}_z$, where $v+w+x+y+z = 100\%$, v is from 10 to 35 atomic%, w is from 10 to 65 atomic%, y is from 10 to 50 atomic%, x is from 1 to 30 atomic%, and z is from 0.1 to 15 atomic%, provided that $x/z > 0.25$, wherein substantially none of the fluorine is bonded to the carbon.

17. The film of claim 16, having a bulk density of less than 1.5 g/cc, a pore size less than 2.5 nm equivalent spherical diameter, as determined by small angle neutron scattering or positron annihilation lifetime spectroscopy, wherein most of the hydrogen is bonded to the carbon, and the film is deposited on a substrate as an insulation layer, an interlayer dielectric layer, an intermetal dielectric layer, a capping layer, a chemical-mechanical planarization or etch stop layer, a barrier layer or an adhesion layer in an integrated circuit.

18. A chemical-vapor deposition method for producing the film of claim 1, said method comprising:

- a. providing a substrate within a vacuum chamber;
- b. introducing into the vacuum chamber gaseous reagents including a fluorine-providing gas, an oxygen-providing gas and at least one

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precursor gas selected from the group consisting of an organosilane and an organosiloxane; and

- c. applying energy to the gaseous reagents in said chamber to induce reaction of the gaseous reagents and to form the film on the substrate.

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19. The method of claim 18, wherein the energy applying comprises supplying plasma power from 0.02 to 7 watts/cm² based upon a surface area of the substrate.

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20. The method of claim 18, wherein the at least one precursor gas is an alkylsilane of the general formula $R^1_nSiR^2_{4-n}$, where n is an integer from 1 to 3; R^1 and R^2 are independently at least one branched or straight chain C_1 to C_8 alkyl group, a C_3 to C_8 substituted or unsubstituted cycloalkyl group, a C_2 to C_{10} partially unsaturated alkyl group, a C_6 to C_{12} substituted or unsubstituted aromatic, a corresponding linear, branched, cyclic, partially unsaturated alkyl, or aromatic containing alkoxy groups, and R^2 is alternatively hydride.

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21. The method of claim 20, wherein the alkylsilane is a member selected from the group consisting of methylsilane, dimethylsilane, trimethylsilane, tetramethylsilane, phenylsilane, methylphenylsilane, cyclohexylsilane, tert-butylsilane, ethylsilane, diethylsilane, tetraethoxysilane, dimethyldiethoxysilane, dimethyldimethoxysilane, dimethylethoxysilane, methyldiethoxysilane, triethoxysilane, trimethylphenoxysilane and phenoxysilane.

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22. The method of claim 18, wherein at least one of the fluorine-providing gas and the at least one precursor has the formula $R^1_nSiF_{4-n}$, where n is an integer from 1 to 3; and R^1 is at least one branched or straight chain C_1 to C_8 alkyl group, a C_3 to C_8 substituted or unsubstituted cycloalkyl group, a C_2 to C_{10} partially unsaturated alkyl group, a C_6 to C_{12} substituted or unsubstituted aromatic, a corresponding linear, branched, cyclic, partially unsaturated alkyl, or aromatic containing alkoxy groups.

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23. The method of claim 22, wherein there is more than one said organosilane, including a fluorinated organosilane.

24. The method of claim 22, wherein at least one of the fluorine-providing gas and the at least one precursor is fluorotrimethylsilane, difluorodimethylsilane methyltrifluorosilane, fluotriethoxysilane or difluorodimethoxysilane.

25. The method of claim 18, wherein the at least one precursor is a linear organosiloxane of Formula I: $R^1(R^2_2SiO)_nSiR^2_3$ where n is an integer from 1 to 10 or a cyclic organosiloxane of Formula II: $(R^1R^2SiO)_n$ where n is an integer from 2 to 10; R^1 and R^2 are independently at least one branched or straight chain C_1 to C_8 alkyl group, a C_3 to C_8 substituted or unsubstituted cycloalkyl group, a C_2 to C_{10} partially unsaturated alkyl group, a C_6 to C_{12} substituted or unsubstituted aromatic, or a corresponding linear, branched, cyclic, partially unsaturated alkyl, or aromatic containing alkoxy groups, and R^2 is alternatively hydride.

26. The method of claim 25, wherein the organosiloxane is selected from the group consisting of 1,3,5,7-tetramethylcyclotetrasiloxane, octamethylcyclotetrasiloxane, hexamethylcyclotrisiloxane, hexamethyldisiloxane, 1,1,2,2-tetramethyldisiloxane and octamethyltrisiloxane.

27. The method of claim 18, wherein at least one of the organosilane and the fluorine-providing gas is a cyclic or linear organosiloxane, which contains at least one Si-F bond.

28. The method of claim 27, wherein there is more than one said organosilane, including a fluorinated organosilane.

29. The method of claim 18, wherein the at least one precursor is a linear organosilane oligomer of the general formula $R^2(SiR^1R^2)_nR^2$ where n is an integer from 2 to 10 or a cyclic organosilane oligomer of the general formula $(SiR^1R^2)_n$, where n is an integer from 3 to 10; R^1 and R^2 are at least one branched or straight

chain C₁ to C₈ alkyl group, a C₃ to C₈ substituted or unsubstituted cycloalkyl group, a C₂ to C₁₀ partially unsaturated alkyl group, a C₆ to C₁₂ substituted or unsubstituted aromatic, or a corresponding linear, branched, cyclic, partially unsaturated alkyl, or aromatic containing alkoxy groups, and R² is alternatively hydride.

5 30. The method of claim 29, wherein the linear organosilane oligomer is selected from the group consisting of 1,2-dimethyldisilane, 1,1,2,2-tetramethyldisilane, 1,2-dimethyl-1,1,2,2-dimethoxydisilane, hexamethyldisilane, octamethyltrisilane, 1,2,3,4,5,6-hexaphenylhexasilane, 1,2-dimethyl-1,2-diphenyldisilane and 1,2-diphenyldisilane.

10 31. The method of claim 18, wherein at least one of the organosilane and the fluorine-providing gas is a linear or cyclic organosilane oligomer with at least one Si-F bond.

 32. The method of claim 31, wherein there is more than one said organosilane, including a fluorinated organosilane.

15 33. The method of claim 18, wherein the at least one precursor is a cyclic alkylsilane, a cyclic alkoxydisilane or contains at least one alkoxy or alkyl bridge between a pair of silicon atoms.

 34. The method of claim 33, wherein the at least one precursor is 1,2-disilanoethane, 1,3-disilanopropane, dimethylsilacyclobutane, 1,2-bis(trimethylsiloxy)cyclobutene, 1,1-dimethyl-1-sila-2,6-dioxacyclohexane, 1,1-dimethyl-1-sila-2-oxacyclohexane, 1,2-bis(trimethylsiloxy)ethane, 1,4-bis(dimethylsilyl)benzene or 1,3-dimethylsilacyclobutane.

20 35. The method of claim 18, wherein the at least one precursor contains a reactive side group selected from the group consisting of an epoxide, a carboxylate, an alkyne, a diene, a phenyl ethynyl, a strained cyclic group and a C₄ to C₁₀ group which can sterically hinder or strain the at least one precursor gas.

36. The method of claim 18, wherein a mixture of more than one said at least one precursor gas is introduced into the vacuum chamber.

37. The method of claim 18, wherein the fluorine-providing gas is selected from the group consisting of SiF_4 , NF_3 , F_2 , HF , SF_6 , ClF_3 , BF_3 , BrF_3 , SF_4 , NF_2Cl ,
5 FSiH_3 , F_2SiH_2 , F_3SiH , organofluorosilanes and mixtures thereof, provided that the organofluorosilanes do not include any F-C bonds.

38. The method of claim 18, wherein the fluorine-providing gas is SiF_4 .

39. The method of claim 18, wherein the oxygen-providing gas is O_2 , N_2O , ozone, hydrogen peroxide, NO , NO_2 , N_2O_4 , or mixtures thereof.

10 40. The method of claim 18, further comprising introducing at least one inert gas into the vacuum chamber.

41. The method of claim 18, further comprising introducing at least one additional reactive substance into the vacuum chamber.

15 42. The method of claim 41, wherein the at least one additional reactive substance is a gaseous or liquid organic substance, NH_3 , H_2 , CO_2 , or CO .

43. The method of claim 42, wherein the organic substance is selected from the group consisting of CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , benzene, naphthalene, toluene and styrene and provides carbon for said reaction.

20 44. The method of claim 18, wherein most of the hydrogen is bonded to the carbon.

45. The method of claim 18, wherein the film has a dielectric constant of less than 3.5.

46. The method of claim 18, wherein the film has a dielectric constant of less than 3.0.

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~~47. The method of claim 18, wherein the film has superior mechanical properties to an OSG film stoichiometrically equivalent to the film but for the absence of fluorine in the OSG film.~~

5 48. The method of claim 18, wherein the film has a density of less than 2.0 g/cc.

49. The method of claim 18, wherein the film has a density of less than 1.5 g/cc.

50. The method of claim 49, further comprising adding a porogen to the gaseous reagents to provide said density.

10 51. The method of claim 18, wherein the film has a pore size less than 5 nm in equivalent spherical diameter, as determined by small angle neutron scattering or positron annihilation lifetime spectroscopy.

15 52. The method of claim 18, wherein the film has a pore size less than 2.5 nm in equivalent spherical diameter, as determined by small angle neutron scattering or positron annihilation lifetime spectroscopy.

53. The method of claim 18, further comprising depositing the film on a semiconductor substrate at a thickness of 0.002 to 10 microns.

20 54. The method of claim 18, further comprising using the film as an insulation layer, an interlayer dielectric layer, an intermetal dielectric layer, a capping layer, a chemical-mechanical planarization or etch stop layer, a barrier layer or an adhesion layer in an integrated circuit.

55. The method of claim 18, wherein the film has an average weight loss of less than 1.0 wt%/hr isothermal at 425°C under N₂.

25 56. The method of claim 18, wherein the film has an average weight loss of less than 1.0 wt%/hr isothermal at 425°C under air.

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57. The method of claim 18, wherein said energy is applied by at least one of a thermal, plasma, pulsed plasma, helicon plasma, high density plasma, inductively coupled plasma, and remote plasma techniques.

5 58. The method of claim 18, wherein said reaction comprises generating a capacitively coupled plasma.

59. The method of claim 18, wherein said film is deposited at a deposition rate of at least 50 nm/min.

60. The method of claim 18, wherein a flow rate for each of said gaseous reagents ranges from 10 to 5000 sccm per single 200 mm wafer chamber.

10 61. The method of claim 18, wherein a pressure in the vacuum chamber is 0.01 to 600 torr.

62. The method of claim 18, wherein a pressure in the vacuum chamber is 1 to 10 torr.

63. The method of claim 18, wherein said film forms a conformal coating.

15 64. The method of claim 18, wherein the film deposited on a non-patterned or smooth surface has a thickness that changes less than 2% over one standard deviation across the substrate with a 10% outermost edge exclusion.

65. The method of claim 18, further comprising post-treating the film after deposition.

20 66. The method of claim 65, wherein said post-treating comprises at least one of thermal treatment, plasma treatment and chemical treatment.

67. The method of claim 18, wherein the film has a bulk density of less than 1.5 g/cc, a pore size less than 2.5 nm equivalent spherical diameter, as determined by small angle neutron scattering or positron annihilation lifetime spectroscopy,
25 wherein most of the hydrogen is bonded to the carbon, and the film is deposited on the substrate as an insulation layer, an interlayer dielectric layer, an intermetal

dielectric layer, a capping layer, a chemical-mechanical planarization or etch stop layer, a barrier layer or an adhesion layer in an integrated circuit.

5 68. The method of claim 18, wherein the gaseous reagents include at least one molecule functioning as at least two of the fluorine-providing gas, the oxygen-providing gas and the at least one precursor gas.

69. The method of claim 18, wherein the gaseous reagents include at least one molecule functioning as the fluorine-providing gas, the oxygen-providing gas and the at least one precursor gas.

10 70. The film of claim 1, said film being amenable to chemical mechanical planarization, aluminum subtractive technology, copper damascene technology or anisotropic etching.

71. The film of claim 1, said film being capable of adhering to silicon, SiO_2 , Si_3N_4 , OSG, FSG, silicon carbide, antireflective coatings, photoresists, organic polymers, porous organic and inorganic materials, metals, and metal barrier layers.

15 *Ryfs* 72. In a method for producing an organosilica glass film comprising chemical vapor deposition of organosilane or organosiloxane to produce the organosilica glass film, the improvement wherein a source of inorganic fluorine codeposits inorganic fluorine during at least a portion of said deposition of the organosilane or organosiloxane to produce a film substantially free of organic fluorine.

20 73. The method of claim 72, wherein the improvement improves a Young's Modulus and a nanoindentation hardness of the film by at least 10% each.

74. The method of claim 72, wherein the improvement improves a thermal stability of the film.

25 75. The method of claim 72, wherein the improvement improves a chemical and environmental stability of the material.